

# Molecular Fragmentation of Acetylene by VUV Double Photoionization <sup>†</sup>

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**Abstract:** Acetylene is a simple molecule of interest for interstellar medium (ISM) and planetary atmospheres. The presence of C<sub>2</sub>H<sub>2</sub> was detected by IR spectroscopic measurements. Acetylene was also found as a minor component in the atmosphere of gas giants like the planet Jupiter, in the atmosphere of Saturn’s satellite Titan, and in comets, where photochemical experiments have demonstrated that this simple hydrocarbon is a likely precursor of C<sub>2</sub>, a widely observed component in such environments. It has to be noted that the presence in planetary atmospheres and ISM of Vacuum Ultra Violet (VUV) light’s photons as well as cosmic rays makes highly probable the double photoionization of molecular species with the production of molecular dications producing subsequent dissociation into ionic fragments having a high kinetic energy content of several eV. This translational energy is sufficient in some cases to allow ions escape from the upper atmosphere of some planet of the Solar System, as Venus, Mars and Titan, into space. In this contribution we present the experimental study of the microscopic dynamics of the two-body dissociation reactions of the C<sub>2</sub>H<sub>2</sub><sup>2+</sup> dication, induced by the double ionization of acetylene molecules by VUV photons in the energy range of 31.9–50.0 eV. The photoionizing agent was a tunable synchrotron radiation beam, while ion products are revealed by coupling photoelectron-photoion-photoion-coincidence and ion imaging techniques. The measured angular distributions and kinetic energy of product ions exhibit significant changes (as the photon energy increases) for the three leading dissociation reactions producing H<sup>+</sup>+C<sub>2</sub>H<sup>+</sup>, C<sup>+</sup>+CH<sub>2</sub><sup>+</sup>, and CH<sup>+</sup>+CH<sup>+</sup>, providing detailed information on the fragmentation dynamics of the C<sub>2</sub>H<sub>2</sub><sup>2+</sup> dication.

**Keywords:** double photoionization; acetylene; synchrotron radiation; molecular dication; planetary atmosphere; ions escape

## 1. Introduction

In gas phase ionization processes can be induced by different collisional processes involving energetic photons, electrons or excited metastable neutral species (in this case we have the so called collisional autoionization, or Penning ionization reactions [1,2]). All ionization reactions play an important role in several phenomena occurring in low energy ionized plasmas [3], in the upper atmosphere of planets, where they govern the chemistry of ionospheres [4,5], and in electric discharges [6,7].

In space, ionic species can be formed in various ways, and the interaction of neutral molecules with cosmic rays, UV photons, X-rays and other phenomena such as shock waves are all important processes for their production. In particular, they can absorb UV photons having an energy content higher than the ionization potential giving rise to the ejection of one or two electrons with the formation of both singly and doubly charged ions, respectively. In the latter case the so called molecular dications are produced. Molecular dications can be formed by different techniques, as mass spectrometry [8], ion-molecule reactions [9], and double photoionization processes [10–13]. They are stable or metastable [8,14] molecular species, and in the latter case they could be used, in principle, as energy storage at a molecular level [8,9,15]. Such doubly charged ionic species can be produced also by cosmic rays, which are significant since they are ubiquitous in space, carrying a large energy content (up to 100 GeV), and consisting of protons, alpha particles, electrons,  $\gamma$ - and X-rays, and (to a small extent) also heavier nuclei (such as  $C^{6+}$ ). For such reasons, molecular dications have been suggested to play a role in the envelope of young stellar objects [16] and upper planetary atmospheres [17–20].

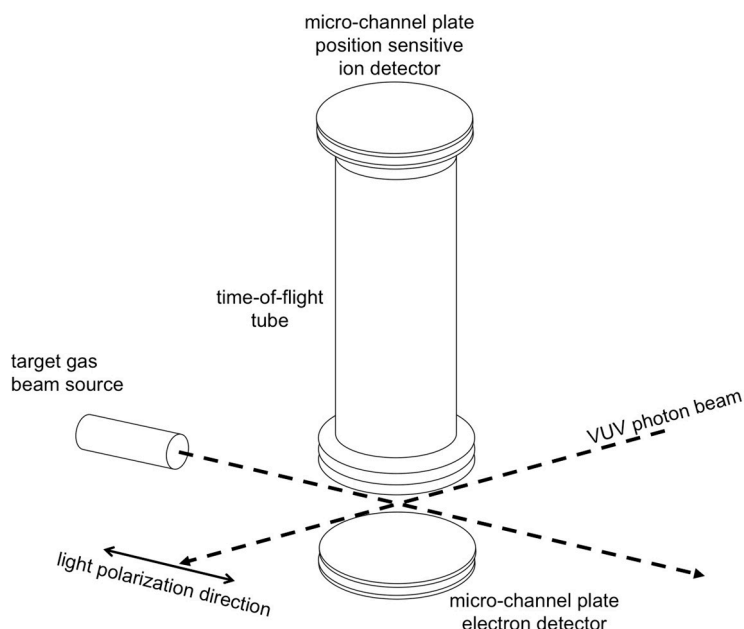
It has to be noted that the double ionization producing a molecular dication can induce Coulomb explosion and fragment ions formation with a high kinetic energy content. For such a reason molecular dications are considered as exotic species, and when they are formed in planetary ionospheres the possibility to generate dissociative products with a kinetic energy of several eV, allows these ionic fragments to reach sufficient velocity to escape into space. Therefore, double ionization processes can in principle contribute to the continuous erosion of the atmosphere of some planets of the Solar System, like Mars and Titan (the largest satellite of Saturn), as discussed in recent papers [21–23]. In the present work is discussed the production of  $C_2H_2^{2+}$  molecular dications by Double Photoionization (DPI) of acetylene molecules characterizing its microscopic dynamical evolution towards the two-body fragmentation channels by the determination of: (i) the angular distribution of product ions; (ii) the kinetic energy with which they are produced by Coulomb explosion. The DPI is a phenomenon in which two electrons are removed simultaneously from an atom or a molecule by the absorption of a single photon. This process is therefore a strong manifestation of electron correlation. The DPI process plays an important role in many fields of natural sciences: from radiation damage of biomolecules, to the study of organic superconductors [24]. Simple hydrocarbons, such as acetylene,  $C_2H_2$ , provides a benchmark for studying this kind of process, owing to the variety of structures they can have. In the present work, we have studied the prototypical  $C_2H_2^{2+}$  organic dication by the use of photoelectron-photoion-photoion coincidence spectroscopy (PEPIPICO) by the use of VUV Synchrotron Radiation. The PEPIPICO results allowed to determine the angular distribution of the photofragments with respect to the incident light polarization vector, and the kinetic energy released in the fragmentation process (KER) as a function of the photon energy.

## 2. Experiments

The data recorded by DPI of acetylene molecules have been recorded at the ELETTRA Synchrotron Light Laboratory (Trieste, Italy) using the ARPES (Angle-Resolved Photoemission Spectroscopy) end station of the Gas Phase Beamline. As mentioned in the previous section, in order to measure the angular distribution of the photofragments with respect to the incident light polarization vector, the KER of final ions, and the lifetime of  $C_2H_2^{2+}$  dications, we used the PEPIPICO coincidence spectroscopy coupled with ion-imaging techniques. Details about the beamline and the end station have been already reported elsewhere [25], and the apparatus used for the experiment

discussed here has also been described previously [26,27]. Therefore, only some features relevant for the present investigation are outlined here.

A tunable monochromatic synchrotron light beam, with a resolution of about 1.5 meV, crosses at right angles an effusive molecular beam of  $C_2H_2$ , and the product ions are then detected in coincidence with photoelectrons. The light polarization vector is parallel to the synchrotron ring plane and perpendicular to the time-of-flight direction of detected ions. Incident photon fluxes and the gas pressure are monitored, and the ion yield has been corrected for flux changes of pressure and photon, when the photon energy was scanned. The used PEPIICO coincidence extraction and detection system (see Figure 1) is fully described in Ref. [28]. Such a device consists in a time of flight (TOF) spectrometer equipped with an ion position sensitive detector, being especially designed in order to properly measure the spatial momentum components of the dissociation ionic products [29]. The analysis of the recorded coincidences distribution (at each investigated photon energy) as a function of the arrival time differences ( $t_2 - t_1$ ) of fragment ions to the ion position sensitive detector (see Figure 1), can provide, by using the procedure already applied in several works [30–32], the following observables: (i) the kinetic energy distributions for each product ion, (ii) the life time of the intermediate molecular dications, and (iii) the angular distributions of final ions coming out from its Coulomb explosion.



**Figure 1.** A scheme of the used electron-ion extraction and detection system used for the PEPIICO measurements (see text).

Acetylene, from a commercial cylinder (with a 99.0% nominal purity) at room temperature, were supplied to a needle effusive beam source.

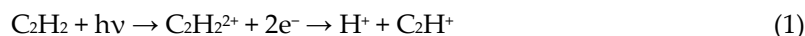
### 3. Results and Discussion

Acetylene is a simple molecule of interest for interstellar medium (ISM) and planetary atmospheres.  $C_2H_2$  was detected in the ISM by IR spectroscopic measurements [33]. Moreover, it was found as a minor component in the atmosphere of gas giants like the planet Jupiter, in the atmosphere of Saturn's satellite Titan [34], and in comets, where photochemical experiments have demonstrated that this simple hydrocarbon is a likely precursor of  $C_2$ , a widely observed component in such environments [33,35,36].

In a previous work [31] we studied the double photoionization of acetylene molecules by using VUV synchrotron radiation at 39 eV photon energy range producing the  $C_2H_2^{2+}$  dication dissociating by Coulomb explosion via three different two-body fragmentation channels producing the following

ion pairs:  $H^+ + C_2H^+$ ,  $CH^+ + CH^+$ , and  $C^+ + CH_2^+$ , whose threshold energies (33.8, 34.0, and 34.0 eV, respectively) were in agreement with previous experimental determinations by Eland and coworkers [37]. In the present work we have focused our attention on the characterization of the  $C_2H_2^{2+}$  microscopic dynamical evolution towards the two-body fragmentation channels by the determination of the angular distribution of product ions, and KER, as a function of the photon energy.

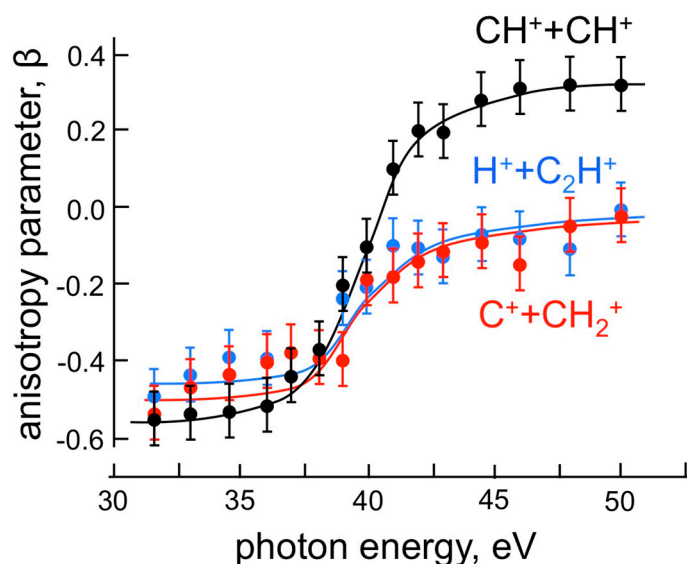
The main dissociation channels observed in the photon energy range investigated (31.9 eV–50.0 eV) are:



The angular distribution of the photofragments follows the relation first introduced by R. N. Zare in 1972 [38], and can provide valuable information about the dissociation dynamics:

$$I(\vartheta)\sin(\vartheta) = \frac{\sigma_{tot}}{4\pi} \left[ 1 + \frac{\beta}{2} (3\cos^2 \vartheta - 1) \right] \quad (4)$$

In Equation (4),  $I(\theta)$  and  $\sigma_{tot}$  are the differential and the total cross section of the process, respectively, while  $\theta$  is the angle between the velocity vector of the fragment ion and the light polarization vector. The  $\beta$  parameter, also called anisotropy parameter, ranges from  $-1$ , for the emission of product ions along a direction perpendicular to the polarization vector, up to a value of  $2$  for a parallel direction. Isotropic distribution of fragment ions is characterized by a value  $\beta = 0$ . The recorded angular distributions obtained in the dissociative double photoionization of  $C_2H_2$  molecules are shown in Figure 2, as a function of the photon energy.

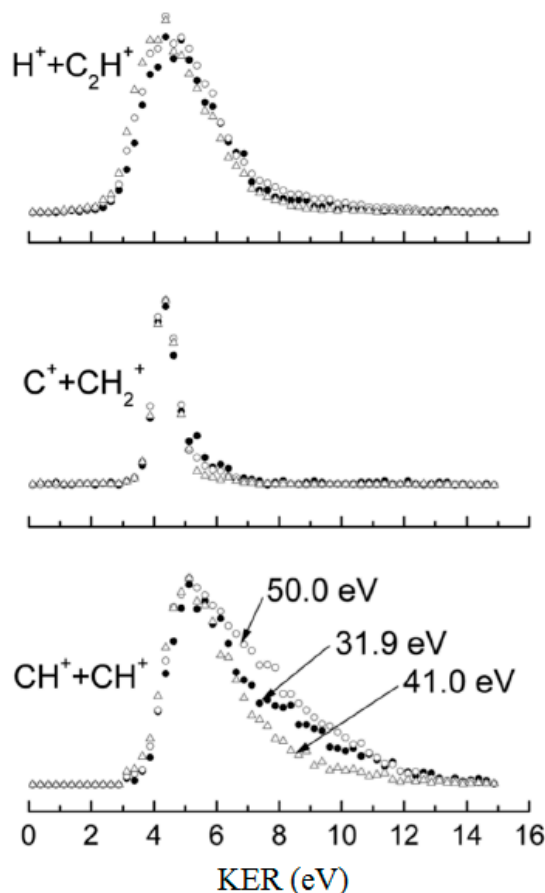


**Figure 2.** Photon energy dependence of the  $\beta$  anisotropy parameter (see Equation (4)) for each two-body fragment ion coming out from the Coulomb explosion of the  $C_2H_2^{2+}$  molecular dication (see reactions 1–3), as measured at a 31.9–50.0 eV photon energy range.

The results obtained in the investigated energy range show an increase of the  $\beta$  values for reaction (1) and reaction (3), from a negative value of about  $-0.5$  to an almost isotropic distribution having  $\beta \approx 0$ , whereas for reaction (2) we observed a change from a negative  $\beta$  value of about  $-0.6$  to a positive one of  $+0.3$  (see Figure 2). These findings are of particular interest because they suggest an

appreciable change in the dissociation mechanism of the dication that control the angular distribution of the final ionic fragments.

The same evidences arise from the KER distributions of the various dissociation channels (see Figure 3). In fact, by analyzing the density distribution of recorded coincidence plots at each investigated photon energy, using the procedure discussed in the previous section, we were able to extract the translational energy distributions of each product ion for reactions 1–3.



**Figure 3.** Total kinetic energy distributions of ion products for the three dissociation channels (see reactions 1–3 in the text) at some representative photon energies.

Such KER distributions as a function of the investigated photon energy are shown in Figure 3. In the case of reaction (3), the total kinetic energy distribution does not change significantly with the photon energy, conversely the reaction (1) exhibits a tail at higher energy, that can be fitted with two Gaussian curves. This is an indication that reaction (1) can occur with two different mechanisms [37,39]: a “slow” dissociation component in which the  $C_2H_2^{2+}$  ion is mainly formed in its ground electronic state, with a lifetime of about 180 ns, and a “fast” dissociation component, above 37 eV, through the formation of a short lived dication in an excited electronic state, with a lifetime shorter than 50 ns. The same effect can be seen in the kinetic energy distribution of reaction (2), the symmetric one, but with a more spectacular pattern, where three components change with the photon energy, suggesting a much more complicated pattern involving several electronic states. This kind of ultrafast processes have been successfully studied, for example, in the case of the isomerisation of acetylene in vinylidene in X-ray FEL time-resolved experiments [40]. The same method could be applied in next future for the study of the dynamic of these ultrafast dissociation processes observed in the double photoionization of the acetylene molecule. Finally, it has to be noted that the translational energy content of each  $H^+$ ,  $C^+$ ,  $CH^+$  and  $CH_2^+$  product ion is quite big, having an average value ranging between 4.0, 2.2, 2.5 and 2.0 eV, respectively. This kinetic energy is sufficient to allow this species participating in the atmospheric escape from Mars and Titan where

they are characterized by a typical escape energy of 0.13 and 0.02 eV (in the case of  $H^+$ ), 1.5 and 0.28 eV (in the case of  $C^+$ ), 1.6 and 0.30 eV (for  $CH^+$ ), 1.8 and 0.32 eV (for  $CH_2^+$ ), respectively [17,21].

#### 4. Conclusions

The two body fragmentation reactions (1)–(3) coming out from the Coulom explosion of the  $C_2H_2^{2+}$  molecular dication produced by DPI using tunable synchrotron radiation in the 31.9–50.0 eV photon energy range, have been studied by combining PEPIICO coincidence and ion-imaging techniques. KER and angular distributions were obtained for all dissociation products. The results indicate a threshold for double ionization of acetylene just below 31.9 eV, in good agreement with the previous determination of 31.7 eV [37]. Above this photon energy value, reactions (1) and (3) occur with a mechanism that appears to involve a few elementary steps through a limited number of electronic states of the intermediate  $C_2H_2^{2+}$  dication. In contrast, reaction (2), occurs with a different microscopic mechanism involving several electronic states of the intermediate dication, and the competition of more dissociation channels. The recorded KER data demonstrate that the fragment product ions  $CH_2^+$ ,  $CH^+$ ,  $C^+$ ,  $H^+$  are characterized by a translational energy ranging between 1.0 and 6.0 eV that is large enough to allow their escape process from the upper atmospheres of Mars and Titan. The studies here presented could be helpful in understanding important details about the chemistry of planetary ionospheres.

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**Author Contributions:** S.F. and S.S. conceived and designed the experiment; all authors performed the experiments; S.F., F.P., M.A., L.S. and F.V. analyzed the data; S.F., M.A., L.S., R.R., and S.S. contributed reagents/materials/analysis tools; S.F. and V.L. wrote the paper.

**Conflicts of Interest:** The author declare no conflict of interest. The founding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

#### Abbreviations

The following abbreviations are used in this manuscript:

ISM	Double Photoionization
VUV	Vacuum Ultraviolet
UV	Ultraviolet
DPI	Double Photoionization
PEPIICO	Photoelectron-Photoion-Photoion-Coincidence spectroscopy
KER	Kinetic Energy Released
ARPES	Angle-Resolved Photoemission Spectroscopy
TOF	Time-of-Flight

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